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DICHOTOMOUS REACTION PATHWAYS IN THE REACTION OF TRIARYLPHOSPHINE OXIDES WITH MEERWEIN'S SALT

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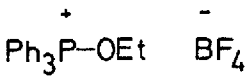
Abstract: Addition of triphenylphosphine oxide to triethyloxonium tetrafluoroborate leads to the formation of ethoxytriphenylphosphonium tetrafluoroborate in high yield, whereas inverse addition yields an oxygen bridged diphosphonium salt.

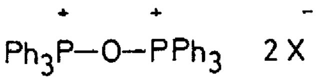
Alkoxyphosphonium salts are compounds of current interest in several laboratories[1] worldwide owing to their intermediacy in various useful synthetic procedures such as the Mitsunobu[2] and Lee[3] reactions. We wish to report here the preparation and isolation of a simple alkoxyphosphonium salt as well as of two oxygen bridged diphosphonium salts isolated in the course of our studies in this area.

Thus addition of a solution of triphenylphosphine oxide (20 mmol.) in dichloromethane (20 ml) to a solution of Meerwein's salt (triethyloxonium tetrafluoroborate)(20 mmol.) in dichloromethane (20 ml) followed by dilution with diethyl ether (60 ml) led to the precipitation of ethoxytriphenylphosphonium tetrafluoroborate[4,5] (1) as a white crystalline solid in 92% yield. Inverse, dropwise addition of Meerwein's salt (20 mmol.) in dichloromethane (20 ml) to triphenylphosphine oxide (21 mmol.) in dichloromethane (20 ml) lead to the *immediate* precipitation of a white solid which was isolated, in 34% yield, by filtration. On the basis of its microanalysis and ^{1}H and ^{31}P nmr spectra this compound was assigned the structure (2)[6]. Dilution of the reaction mixture, after filtration, with diethyl ether caused precipitation of (1) (50% isolated). The trifluoromethanesulphonate analogue (3) of (2) has been previously prepared[7] by treatment of triphenylphosphine oxide with trifluoromethanesulphonic anhydride and is widely used as a dehydrating agent in organic synthesis, nevertheless its ^{31}P nmr characteristics have not been reported to date. In our hands dichloromethane solutions of (2) and (3) had identical ^{31}P nmr spectra (δ + 73.7) indicating that they differ simply in the counter ion.



$Ph_3\overset{+}{P}{-}OEt \quad \overset{-}{BF_4}$

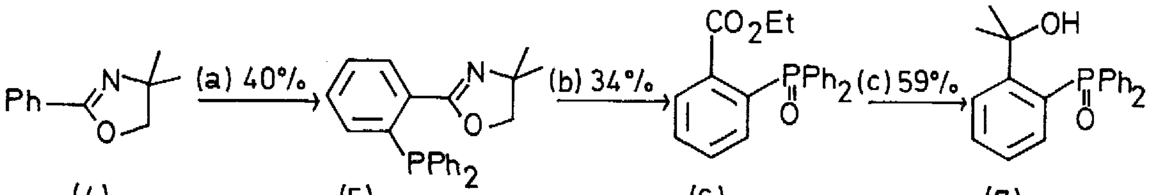
(1)



$Ph_3\overset{+}{P}{-}O{-}\overset{+}{P}Ph_3 \quad 2\overset{-}{X}$

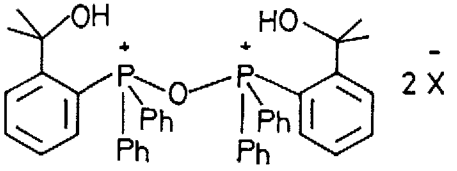
(2) $\overset{-}{X}=\overset{-}{BF_4}$; (3) $\overset{-}{X}=C\overset{-}{F_3SO_3}$

In a further reaction the triarylphosphine oxide (7)[8], prepared from 2-phenyl-4,4-dimethyl-2-oxazoline (4) by the sequence outlined in the scheme, gave on addition to Meerwein's salt the diphosphonium salt (8) in 67% isolated yield. The same result was observed regardless of the mode of addition of the reagents. Reaction of (7) with trifluoromethanesulphonic anhydride gave the corresponding trifluoromethanesulphonate (9).


(4) (5) (6) (7)

(a) *n*BuLi, Et_2O, 0 °C; Ph_2PCl. (b) EtOH, *c*H_2SO_4, Δ. (c) MeMgI, Et_2O.

Scheme


(8) $X^- = BF_4^-$

(9) $X^- = CF_3SO_3^-$

Evidently whilst alkoxyphosphonium salts such as (1) can be isolated as white crystalline solids by application of the correct experimental proceedures they undergo ready nucleophilic attack at phosphorus by phosphine oxides to give oxygen bridged diphosphonium salts and not at carbon as they are required to do with other oxygen centred nucleophiles when postulated as intermediates in the Mitsunobu reaction.

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2. O. Mitsunobu, *Synthesis,* 1. (1981)
3. R. Appel, *Angew. Chem. Int. Ed. Engl., 14,* 801. (1975)
4. Ethoxytriphenylphosphonium tetrafluoroborate (1): mp 133-134 °C (CH_2Cl_2/Et_2O); ^1H nmr ($CDCl_3$, 400MHz) δ: 1.49 (3H, dt, $J_{PH}{}^{4}$ = 1.2Hz, J_1 = 7Hz), 4.44 (2H, quint., $J_{PH}{}^{1}$ = 7Hz, J_1 = 7Hz), 7.78 (12H, m), 7.89 (3H, m); ^{31}P nmr (CH_2Cl_2) δ: + 61.7[5] (Found: C, 60.97; H, 5.16. Calc. for $C_{20}H_{20}BF_4OP$: C, 60.95; H, 5.11%).
5. Literature ^{31}P nmr δ + 62 for a sample generated *in situ:* D.B. Denney, D.E. Denney and L.A. Wilson, *Tetrahedron Lett.,* 85. (1968)
6. Oxobis(triphenylphosphonium) tetrafluoroborate (2): mp 241-245 °C (CH_2Cl_2/Et_2O); ^1H nmr ($CDCl_3$, 60MHz) δ: 7.5 (m); ^{31}P nmr (CH_2Cl_2) δ: + 75.9 (Found: C, 62.47; H, 4.45. Calc. for $C_{36}H_{30}B_2F_8OP_2$: C, 61.47; H, 4.30%).
7. A. Aaberg, T. Gramstad and S. Husebye, *Tetrahedron Lett.,* 2263. (1979); J. B. Hendrickson and S.M. Schwartzman, *ibid,* 277. (1975)
8. Hydroxyphosphine oxide (7): mp 149-150 °C (EtOH); ^1H nmr ($CDCl_3$, 200MHz) δ 1.64 (6H, s), 7.10 (2H, m), 7.49 (12H, m); ^{31}P nmr ($CDCl_3$) δ: + 41.1; $\bar{\nu}$ (KBr) 3250, 1172; *m/z*: 321 (M^+-CH_3, 100%), 319 (M^+-OH, 15%), 303 (M^+-CH_3-OH, 17%), 277 ($M^+-C(CH_3)_2OH$, 15%). (Found: C, 74.28; H, 6.38. Calc. for $C_{21}H_{21}O_2P$: C, 74.99; H, 6.29%).
9. Diphosphonium tetrafluoroborate (8): mp 158-160 °C (CH_2CH_2/Et_2O); ^1H nmr ($CDCl_3$, 60MHz) δ: 1.96 (12H, s), 7.8 (28H, m); ^{31}P nmr ($CDCl_3/CH_2Cl_2$) δ: + 73.7 (Found: C, 61.15; H, 4.97. Calc. for $C_{42}H_{42}B_2F_8O_3P_2$: C, 60.75; H, 5.10%).

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